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Equilibrium and kinetic studies of biosorption of Cr (III) and Cd (II) by activated carbon prepared from Spirulina algae

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Abstract

The Spirulina algae were converted into activated carbon to remove heavy metal by low cost and innocuous material in the water. The sorption behavior of Chromium (III) and Cadmium (II) cations by Spirulina was studied to uptake the heavy metal cations from aqueous solution. The removal of these metals was investigated by batch method experiment. The main factors that affect Cd^{2+} and Cr^{3+} sorption on Spirulina, the influences of pH (2–7) and contact time (5-120 min) have been investigated. The percent removal of Cr^{3+} and Cd^{2+}cations reached maximum at 35 and 45 min respectively. The binding sorption sites were strongly influenced by pH and the optimum pH for Cd^{2+} and Cr^{3+}cations were 5. The percentage of up taking Cr^{3+} and Cd^{2+}cations reached maximum to 94.3% and 83.8%, respectively. The sorption efficiency of activated carbon prepared from Spirulina for chromium is greater than cadmium metal and the Langmuir module is fitted the results better than other models. Kinetic studies presented that a pseudo-second order model was more appropriate than the pseudo first order model. It is concluded that the activated carbon prepared from Spirulina cloud be used as an effective sorbent for uptake of Cr^{3+} and Cd $^{2+}$ from wastewater.

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Introduction

The contamination of heavy metals of the environment is considered one of major concern due to the tendency of bio-accumulation and their toxicity to the environment and human life. Although ordinary methods for removing heavy metal can be used for water treatment, all methods have advantages and limitation (Khambhaty *et al.*, 2009). The uses of bio-sorbents of biological source have been considered in the last years as one of the most favorable alternatives to normal heavy metal removing strategies. It is easy to prepare, a reliable, and no formation of secondary compounds which could be toxic, low cost and efficient. Besides it can remove different kinds of contaminants. The algae have several features that make them perfect for removing heavy metals. They contain high tolerance to heavy metals, ability to grow both autotrophically and heterotrophically, large surface area, phototaxy, phytochelatin expression and potential for genetic manipulation (Preetha and Viruthagiri 2007). Many researchers have been done on the removal of heavy metal by algae, marine algae, bacteria, yeast and higher plants. Further, this process can remove/ minimize different types of pollutants and thus have wider applicability in water pollution control (Mulbry *et al.*, 2008; Haq *et al.* 2009; Godos *et al.*, 2010; Li and Lee 2012). It is mainly the cell wall of algae is responsible for the phenomenon of biosorption. The cell wall includes carboxyl, hydroxyl, carbonyl, sulfone, sulphonate, amine, and phosphoryl groups (Achak*et al.*, 2009). This leads that the algae has amphoteric features depending on the pH (Chojnacka *et al.*, 2005 and Chojnacka 2009). The object of this work was to utilize Spirulina algae for the preparation of activated carbon through chemical activation using an activating agent. The chemical activated prepared by Spirulina algae was applied for determining the sorption efficiency of Cr (III) and Cd (II). In this work, Kinetics and isotherm studies were used.

Materials and methods

Preparation of the sorbate

Inorganic chemicals were provided by Merck as analytical grade reagents and deionized water were used. The heavy metals studied were Cd (II) and Cr (III). The stock solutions were prepared of cadmium and chromium using their chloride, $CdCl_2.2H_2O$ and $CrCl_3.6H_2O$, respectively, in deionized water.

Preparation of the biosorbent

The Spirulina algae was exposed impregnation in 1dm^{3}of 3 molar H_3PO_4 at 80 °C for 3 hr. Later, it was washed with deionized water till its pH value was 7. The Spirulina was dried at 100 °C for 24 hr. Then in a muffle furnace the dried algae were carbonized at 450 and 700°C for 2 hr (Barnstead, IA U.S.A.). After that, charcoal was crushed and sieved to a size 83-107 µm to obtain the activated carbon of Spirulina algae (ACSA).

Batch sorption studies

The sorption experiment of metal ions by modifying Spirulina was done using the batch experiment. Batch methods were carried out with 100 ml of solutions of heavy metal of 10 and 100 mg/ l at constant temperatures (25 °C) in 250 ml plastic bottles. Different amount of Spirulina were added in the bottles.

After the bottles were placed in a shaker for 6 h (150 rotations per minute (rpm)), the solutions of heavy metals were filtered. The concentrations of heavy metal ions were measured by AAS.

Kinetics study

Kinetics experiments were studied with 10 mg/l of solution in 1L water and with 1 g of Spirulina algae at room temperature (25°C). Water was agitated at 150 rpm for 3 hours. At various intervals 5ml of samples were taken and filtered and analyzed. The kinetics results were estimated with pseudo-first-order, pseudo-second-order and Reichenberg equation. All graphs were plotted by sigma plot program

Results and discussion

Sorption of heavy metals by algal mainly depends on many factors like the initial concentration of metals, the amount of algae and the pH of the solution.

Effect of pH

The pH of the heavy metals solution is one of the vital factors controlling the sorption of the metal ions (Hashem, 2007). The effect of pH on sorption on heavy metal was carried out in the range of 2-7. From (Fig.1), with activated carbon from algae used as sorbent, it was shown that with an increase in the pH of the solution, the percentage removal of metal ions increased up to the maximum removal were obtained at pH 6. The increase in concentration of removal of heavy metals at higher.

Isotherm models

The sorption results have been exposed to different sorption isotherm models, Langmuir, Freundlich and Reichenberg.

Freudlich

The Freundlich sorption isotherm, one of the most broadly used mathematical models, generally describe the experimental data. This isotherm gives an expression covering the surface heterogeneity and the exponential distribution of active sites and their energies (Freundlich, 1906). The Freundlich sorption model was also applied to the uptake of heavy cations (Fig. 2).

$$q_e = K_d C_e^{1/n} \qquad (1)$$

For linearization of the data, the Freundlich equation can be expressed in logarithmic form.

$$log q_e = log K_d + {}^{1}/_{n}\, log C_e \qquad (2)$$

Where C_e is the equilibrium concentration in mg/l. K_d is a constant depend on the temperature and low values of it refer that large amount of the metal exist in solution, however high values refer that the metals have been kept by sorption to the sorbent (Ogata *et al.*, 2014). 1/ n is a characteristic parameter of the sorption system. The smallest value of 1/n (less than 0.5) indicates strong cohesion between the sorbate and sorbent. The constants K_d and 1/n were obtained (Table 1).

Table 1. Isotherms constants of adsorption of Cr (III) and Cd (II).

	Cr	Cd
Frundlich		
K_d(mg/g)	6.39	4.36
1/n	0.057	0.005
R^2	0.94	0.95
Langmuir		
X_m(mg/g)	9.77	4.5
b (l/mg)	0.13	1.09
R^2	0.987	0.99
Temkin		
B_T(KJ/mol)	1.62	0.073
K_T(l/mg)	0.54	1.77
R^2	0.866	0.955

This model does not foretell any saturation of the algae by the heavy metals solution.

The values of 1/n Cr (III) (0.057) in relation to Cd (II) (0.005) (Fig. 2) donate the favored sorption of Cr (III) than Cd (II) perhaps due to its smaller ionic radius indicates the capability of the Spirulina to remove these heavy metals cations from water even at high concentrations (Bhattacharya & Gupta, 2008), indicate that Cr (III) has a better sorption tendency to

Spirulina than the Cd (II) metal. The smaller the hydrated radius cations are the higher attraction for sorption onto the Spirulina. From Freundlich constant 1/n is less than 0.5. This indicates the sorption of Cr (III) and Cd (II) is favorable to Spirulina algae.

Langmuir

The isotherm Langmuir explains the equilibrium distribution of metal ions between the solid and liquid phases (Langmuir, 1918). This model supposes that sorption occurs at definite homogeneous active sites (energetically and identical equal) within the sorbent (Karri *et al.*, 2008). This means that once the active sites occupied no more sorption happen at that active site and the sorption reach saturation.

Table 2. Kinetic parameters for adsorption of Cr (III) and Cd (II).

	Cr	Cd
First-pseudo-order		
q_e(mg/g)	10.3	9.2
K_1(min^{-1})	0.022	0.042
r^2	0.94	0.91
Second-pseudo-order		
K_2(g/mg.min)	$2.25*10^{-4}$	$5.7*10^{-4}$
q_e(mg/g)	6.6	4.6
r^2	0.99	0.99

Heavy metals have been correlated with the Langmuir isotherm.

$$q_{e=}\frac{q_{max}bC_e}{1+bC_e} \qquad (3)$$

This equation can be arranged to:

$$\frac{1}{q_e} = \frac{1}{X_m} + \left(\frac{1}{C_e}\right) + \left(\frac{1}{bX_m}\right)$$

(4)

Where C_e is the equilibrium concentration of heavy metal in solution, q_e is the amount of heavy metals sorbed onto algae. X_m and b are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity X_m represents monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and should vary with temperature. A linear plot is gotten when $1/q_e$ is plotted various $1/C_e$ over the entire concentration of heavy metals studied (Chaturvedi and Sahu , 2014). The value of b of Cr is lower than Cd indicate that the particles radius of Cr are smaller than Cd (Fig. 3).

The Langmuir isotherm model constants and the statistical fits of the sorption data are given in Table (1).

Temkin isotherm

The Temkin (Temkin and Pyzhev, 1940) sorption isotherm model was selected to estimate the sorption potentials of the sorbent. Temkin isotherm is depending on the hypothesis that coverage of sorbent due to sorbate/sorbent which will increase linearly with decrease heat of sorption (Yu and Ya-Juan, 2008). The Temkin sorption is recognized by a uniform allocation of the bonding energies up to some maximum binding energy.

$$q_e = \frac{RT}{b}\ln\left(K_T C_e\right) \qquad (5)$$

By linearisedTemkin equation:

$$q_e = B_T lnK_T + B_T lnC_e \qquad (6)$$

Where $B_T = \frac{RT}{b}$

where K_T (L/g) is the equilibrium binding constant, related to the variation of sorption energy, b_T is a constant corresponding to the heat of sorption, T is the absolute temperature (K), and R is the universal gas constant (8.315 J mol^{-1} K^{-1}). The Temkin isotherm plot for the two heavy metal cations are shown in (Fig. 4) and the isotherm constants are given in Table (1).

From the values of R² in the table (1), it is indicated that the Langmuir isotherm fitted the sorption data.

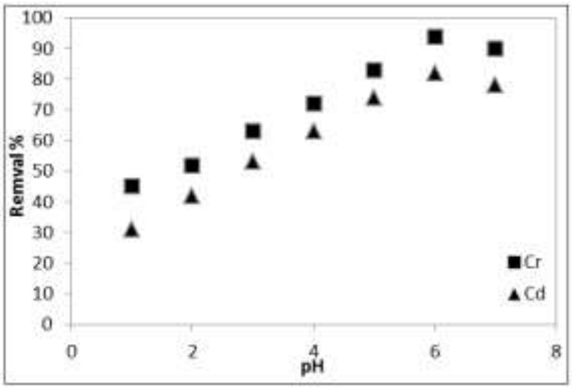

Fig. 1. Effect of pH on the sorption of Cr (III) and Cd (II) on to activated carbon prepared from Spirulina algae.

Kinetics analysis

The kinetic analysis is very significant to determine the controlling rate mechanism of the sorption process of the solid-liquid interface (Acharya *et al.,* 2009).

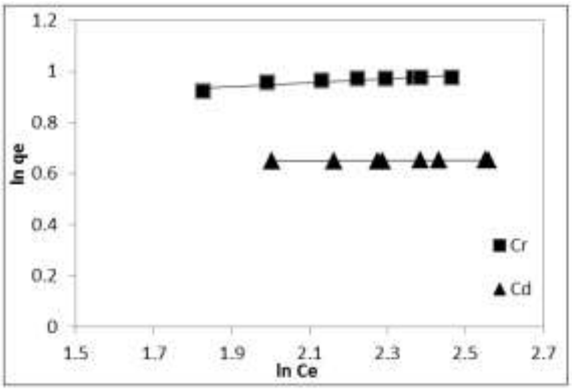

Fig. 2. Freundlich isotherm for sorption of Cr (III) and Cd(II) on to activated carbon prepared from Spirulina algae.

The transformation of the heavy metal from sorbate to the surface of biosorbet could be done in three steps; one or more of them can be the controlling rate mechanism 1) mass transfer from the bulk solution of sorbate over the boundary layer film to biosorbent surface (2) diffusion of the surface to the pores of biosorbent (3) interaction (chemical or physical) of sorbate with the active sites on the surface (internal or external) of biosorbet, and this step is usually supposed to be very fast.

Effect of contact time

The effect of contact time on removal of heavy metal is one of controlling factor of sorption. It was studied for a period of 120 min. 1g of the sorbents was added into different bottles 250 mL of heavy metals, the bottles were closed and shaken in shaker for different contact times chosen (5, 10, 20, 30, 40, 60, 80,100 and 120 minutes). Each bottle was filtered and measured after that. The relationship between the percentage removal of heavy metals from solution and the contact time with activated carbon produced from algae shown in figure 5. From figure, the time required to complete sorption are 35, 45 mints for Cr (III) and Cd (II) respectively. The sorption was rapid at first fast Fig (5) shows that the amount of heavy metals adsorbed by Spirulina increases by increasing the time till the equilibrium occurred. At the beginning of the sorption, the uptake of heavy metals happened rapidly because of active sorption sites. Over time these sites occupied and sorption reaches to the equilibrium (Rifaya *et al.,* 2012 and Mahmoud *et al.*, 2015).The time required to achieve this state of equilibrium of metal indicates the sorption capacity of sorbent under experimental conditions.

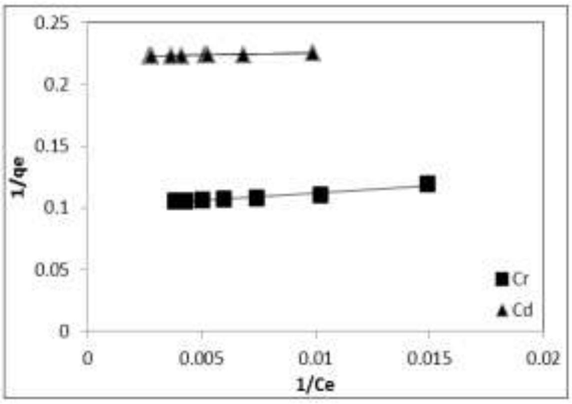

Fig. 3. Langmuir isotherm for adsorption of Cr (III) and Cd (II) on activated carbon prepared from Spirulina algae.

First pseudo order

In order to investigate the controlling mechanism the pseudo first order and pseudo second order are used.

By analyzing the sportive removal of heavy metals from solution at different time, the kinetics of sorption was measured (Ewecharoen *et al.*, 2009). The general expression for pseudo-first-order equation model is shown in equation (7) and (8):

$$\frac{dq}{dt} = K_1(q_e - q_t) \tag{7}$$

The sorption capacities at equilibrium and at time t are expressed by q_e and q_t respectively and k_1 is the pseudo-first order sorption rate constant. After integration, t = 0 to t = t and q_t =0 to q_t = q_t, the integrated form of the equation becomes

$$log(q_e - q_t) = logq_{e-\frac{K_1t}{2.303}} \tag{8}$$

By plotting log (q_e-q_t) against t is straight line the intercept is log q_e and the slope is $K_1/2.303$. Where q_t and q_e are the sorption capacity at equilibrium and time t respectively.

The pseudo-second order chemisorptions kinetic rate equation is expressed as shown in equation

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \tag{9}$$

$$\frac{dq}{(q_e-q_t)} = K_2t \tag{4}$$

By integration this equation

$$\frac{t}{q} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}t \tag{10}$$

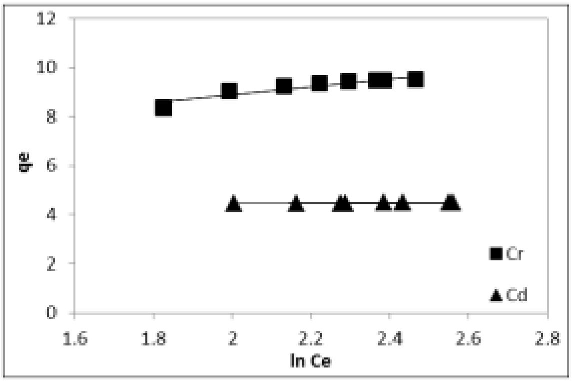

Fig. 4. Temkin isotherm for adsorption of Cr (III) and Cd(II) on activated carbon prepared from Spirulina algae.

The sorption capacities at equilibrium and at time t are represented by q_e and q_t respectively and k_2 is the rate constant of the pseudo-second order sorption.

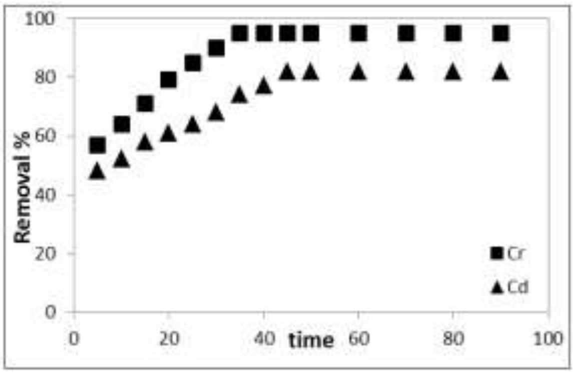

Fig. 5. Effect of time on the sorption of Cr (III) and Cd (II) on activated carbon prepared from Spirulina algae.

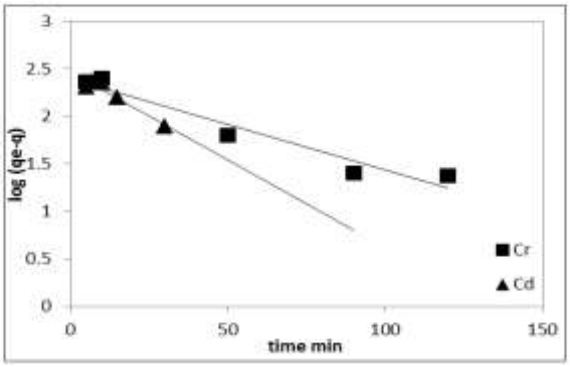

Fig. 6. Pseudo first order kinetics adsorption of Cr (III) and Cd (II) on activated carbon prepared from Spirulina algae.

The results showed the fitted data in figure (7). The sorption of heavy cations data are well represented by the pseudo-second order. Kinetics results expected that the suitability, effectiveness and applicability of pseudo-second order-kinetic model were more than that of the pseudo-first order kinetic model.

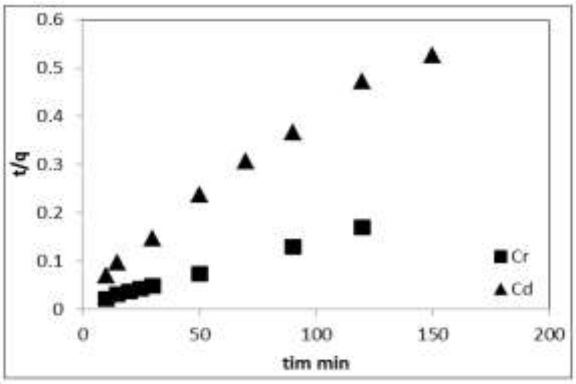

Fig. 7. Pseudo second order kinetics sorption of Cr (III) and Cd(II) on activated carbon prepared from Spirulina algae.

This support the hypothesis of the rate limiting step of sorption may be chemical sorption or chemisorptions (Demirbas *et al.*, 2009). In chemisorptions, the metal ions sorbed on the sorbent surface by making a chemical bond and tend to detect sites that maximize their coordination number with the surface (Babalola, *et al.* 2009). The kinetic constants determined from the slopes and intercepts of the linear plots are shown in table 2.

Reichenberg model

The rate of sorption can be determined by the equation of the mass transfer and diffusion phenomena for the fast reaction, the sorption may be due to film diffusion. To define the step controlling of sorption rate, regarding to Boyd *et al. (*1947) and Reichenberg (1953) the effective particle diffusivity of heavy metal cations may be represented by the equation:

$$f(t) = \left(1 - \frac{6}{\pi^2}\right) e^{-BT} \quad (11)$$

The equation can be represented as:

$$B_t = -0.4977[1 - f(t)] \quad (12)$$

By using $B_t = \frac{\pi^2 D_i}{R^2}$

Where F (t) = q_t/q_e is the fractional attainment of equilibrium at time t, D_i is the effective diffusion coefficient of adsorbates in the adsorbent phase (m^2/s), r is radius of the adsorbent particle assumed to be spherical (m). As presented in Fig. 8. By plotting Bt vs. time a straight line is obtained and the slope will be $\pi^2 D_i / R^2$. The effective diffusivity is almost independent of q_e and the value of D_i largely depends on the properties of the adsorbent, and to some extent on the adsorbate (Sirvastava, *et al.*, 2007). This model was used to differentiate between diffusion controlled sorption and the film diffusion. This proposes sorption rate is governed by the particle diffusion mechanism; it is controlled by film diffusion (Singh *et al.*, 2003). This phenomenon proposes involvement of particle diffusion and film diffusion mechanisms as the rate-controlling step for removal. If the diffusion steps are slow, they become the rate-determining step in the binding to the active sites. The sorption is at random due to the existence of active sites with different energies (Vijayaraghavan and Yun, 2008). From the fig (8) there is linear relation between Bt and t with intercept indicates that either the chemical reaction or diffusion.

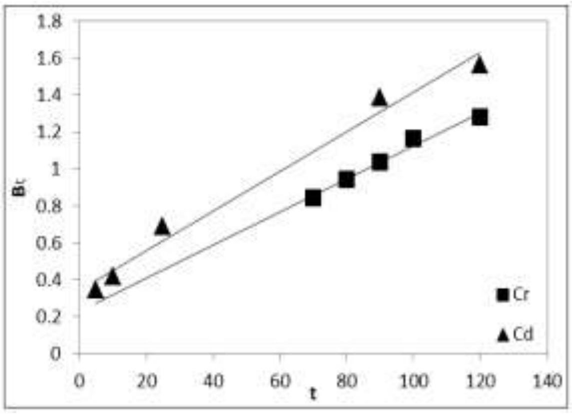

Fig. 8. Reicherberg isotherm for sorption of Cr (III) and Cd (II) on to activated carbon prepared from Spirulina algae.

Conclusion

The sorption isotherms of solute are fitted by Langmuir model. From the obtained results, it is evident that activated carbon produced from Spirulina is a good sorbent for removal of chromium and cadmium. It is cheap and readily available method, thus this study provides a cost effective means for removing metal ions from contaminated water or effluents. Batch experiments were conducted and showed that the sorption is time dependent, pH dependent. The data were studied by four sorption isotherms: the Freundlich, Langmuir, Temkin and

Reichenberg model. Estimating the correlation coefficients for fitting the analytical results presented that the Langmuir isotherm fitted the data more than others. The activated carbon sorbed Cr more than Cd from aqueous solution. The sorption data of Cr (III) and Cd (II) ions on activated carbon indicated that the pseudo second order model was more appropriate than the pseudo-first order model. According to the results, the activated carbon prepared from Spirulina can be used for elimination of heavy metal from aqueous solution as it is of low cost, a locally available and plentiful sorbent.

References

Achak M, Hafidi A, Ouazzani N, Sayadic S, Mandi L. 2009. Low cost biosorbent "banana peel" for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies. Journal of Hazardous Material **166,** 117-125.

Acharya J, Sahu JN, Mohanty CR, Meikap B. 2009. Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. Journal of Chemical Engineering **149,** 249-262.

Babalola J, Babarinde N, Popoola A, Oninla V. 2009. Kinetic, isothermal and thermodynamic studies of the biosorption of Ni (II) and Cr (III) from aqueous solutions by Talinumtriangulare (Water Leaf). The Pacific Journal of Science and Technology **10,** 439-450.

Bhattacharya K, Gupta S. 2008. Kaolinite and montmorillonite as adsorbents for Fe(III), Co(II) and Ni(II) in aqueous medium. Journal of Applied Clay Science **4,** 1-9.

Chojnacka K, Chojnacki A, Górecka H. 2005. Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue–green algae Spirulina sp.kinetics, equilibrium and the mechanism of the process". Journal of Chemotherapy **59,** 75–84.

Chaturvedi D, Sahu O. 2014. Adsorption of Heavy Metal Ions from Wastewater. Global Journal of Environmental Science and Technology **2(3),** 020-028.

Chojnacka K. 2009. Biosorption in Biosorption and bioaccumulation in practice, Nova Science Publishers, Inc., New York, NY, USA, chapter **2(2),** 5–15 .

Ewecharoen A, Thiravetyan P, Wendel E, Bertagnolli H. 2009. Nickel adsorption by sodium polyacrylate-grafted activated carbon. . Journal of Hazardous Material **171,** 335-339

Demirbas E, Dizge N, Sulak MT, Kobya M. 2009. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. Journal of Chemical Engineering **148,** 480-487.

Freundlich HZ. 1906. Over The Adsorption in Solution. Journal of Physical Chemistry **57A,** 385-470.

Gheju M, Miulescu A. 2008 Kinetics of hexavalent chromium adsorption on granular activated carbon. Chemical Bulletin"POLITEHNICA" University (Timisoara) **5,** 1-2.

Godos T, Vargas V, Blanco S, Gonzalez M, Soto R, Garcia-Encina P, Becares E, Munoz R. 2010. A comparative evaluation of microalgae for the degradation of piggery wastewater under photosynthetic oxygenation. Journal of Bioresource Technology **101,** 5150– 5158.

Haq N, Arain M, Haque Z, Badar N, Mughal N. 2009. Drinking water contamination by chromium and lead in industrial lands of Karachi. Journal of Pakistan Medical Association **59,** 270-274.

Hashem A. 2007. Adsorption of Lead Ion from Aqueous Solution by Okra Wastes. International Journal of Physical Science, 2, 178-184.Karri K, Saper R Kales , 2008 Lead Encephalopathy Due to

Traditional Medicines. Journal of Current Drug Safety **3,** 54-59.

Khambhaty Y, Mody K, Basha S, Jha B. 2009. Biosorption of inorganic mercury onto dead biomass of marine Aspergillusniger: Kinetic, equilibrium, and thermodynamic studies. Journal of Environmental Engineering Science**26,** 531-539.

Langmuir I. 1918. The Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum. J.A.M. . Journal of Chemical Society **40,** 1361-1403.

Li C, Lee Y. 2012. Household cyanobacteria Bio-reactor to diminish kitchen waste sewage malodor and produces fertilizer. International Journal of Applied Science and Engineering **10,** 29–39.

Mahmouda M, Ibrahima F, Seham Shabanb A, Youssefa N. 2015. Adsorption of heavy metal ion from aqueous solution by nickel oxide nano catalyst prepared by different methods. Egyptian Journal of Petroleum. **24(1),** 2015, 27–35.

Murali O, Mehar S. 2014. Bioremediation of heavy metals using Spirulina. Journal of Earth and Environmental Sciences **4,** 244–249.

Mulbry W, Kondrad S, Buyer J. 2008. Treatment of dairy swine manure effluents using freshwater algae: fatty acid content and composition of algal biomass at different manure loading rates. Journal of Applied Phycology **20,** 1079–1085.

Ogata F, Kangawa M, Iwata Y, Ueda A, Tanaka Y, Kawasaki N. 2014. A Study on the Adsorption of Heavy Metals by Using Raw Wheat Bran Bioadsorbent in Aqueous Solution Phase. Journal of Chemical & pharmaceutical Bulletin **62(3),** 247–253.

Preetha B, Viruthagiri T. 2007. Bioaccummulation of chromium (VI), copper (II) and nickel (II) ions by growing Rhizopusarrhizus. Journal of Biochemical Engineering **34,** 131-135.

Reichenberg D. 1953. Properties of Ion-Exchange Resins in Relation to their Structure. III. Kinetics of Exchange. Journal of the American Chemical Society. **75,** 589-597.

Rifaya N, Theivasanthi T, Alagar M. 2010. Chemical Capping Synthesis of Nickel Oxide Nanoparticles and their Characterizations Studies Center for Research and Post Graduate Department of Physics, Ayya Nadar Janaki Ammal College, Sivakasi – 626124, Tamilnadu, India.

Temkin M, Pyzhev V. 1940. Kinetics of ammonia synthesis on promoted iron catalysts. Journal of Acta Physico-Chimica Sinica **12,** 217-222.

Vijayaraghavan K, Yun Y. 2008. Bacterial biosorbents and biosorption. Journal of Biotechnology Advances **26,** 266-291.

Yu L, Ya-Juan L. 2008. Biosorption isotherms, kinetics and thermodynamics. Journal of Separation and Purification Technology **61,** 229-242.